氏　　名	りゅう　こくこく 劉　蟈蟈
学位の種類	博　　士（工学）
学位記番号	富理工博甲第 149 号
学位授与年月日	平成 30 年 9 月 28 日
専　攻　名	ナノ新機能物質科学専攻
学位授与の要件	富山大学学位規則第 3 条第 3 項該当
学位論文題目	New Catalysts Development for Gas-To-Liquid Technology （Gas-To-Liquid 技術の新規触媒開発）

論文審査委員

（委員長）	阿部　孝之
	椿　範立
	米山　嘉治

学位論文内容の要旨

学位論文題目　New Catalysts Development for Gas-To-Liquid Technology

（Gas-To-Liquid 技術の新規触媒開発 ）

ナノ新機能物質科学 専攻

氏名　劉蟈蟈（Guoguo Liu）

As rapid increase in population, there are more and more requests for energy by industrialization. The dependence on fuels and chemical feedstocks to solve the energy consumption has created energy crisis and environment issues, such as the production of a large number of greenhouse gases, resulting in greenhouse effect destroys the natural environment. The reduction and transformation of greenhouse gases such as methane and carbon dioxide to other value-added chemicals have received great interest in recent years. Catalytic dry reforming of methane (DRM, $CO_2+CH_4 \rightarrow 2CO+2H_2$) is an efficient route for the conversion of both greenhouse gases into syngas (H_2 and CO). The produced syngas with a high CO content (H_2/CO ratio close to 1.0) is suitable for the production of many valuable chemicals.

In addition, the gradual depletion of crude oil resources and increasing environmental concerns have driven a worldwide research on alternative processes for the production of fuels and commodity chemicals. Fischer-Tropsch synthesis (FTS) has received more attentions than ever since it is considered as an effective process to produce wide-range liquid hydrocarbon fuels and high-value added chemicals from relatively abundant resources, such as natural gas, coal and biomass, via synthetic gas (H_2+CO). Iron based catalysts are considered to be more promising than other metal

catalysts (such as Co and Ru). Because of the Iron-based catalysts have the advantages of low prices, relative low methane selectivities, high water-gas shift (WGS) activities and wide operating temperature ranges, are more promising for FTS, especially in Coal to Liquids (CTL), Biomass to Liquids (BTL) and Gas to Liquids (GTL) processes.

It is well know that methane is a large component of natural gas, wich is abundant and thus a low cost. So, various research is being converted methane in to hydrocarbons or liquid fuels by Gas to Liquids (GTL) processes. Generally, the GTL process have two basic types: (a) direct produce to methanol and (b)via methane reforming method to convert methane into syngas via , and then by Fischer-Tropsch synthesis (FTS) to convert syngas to liquid fuels and hydrocarbons.

In chapter 1, A silicon carbide (SiC) foam monolith decorated with a carbon nanofibers (CNFs) layer was employed as the catalyst support for Ni-based catalyst preparation, used for the CO_2 dry reforming of methane (DRM) reaction. The loading amount of CNFs on the SiC foam monolith was 6.6 wt.%, which obviously increased the surface area of the pristine SiC foam from 4 m^2/g to 24 m^2/g. The prepared CNFs layer strongly attached to the pristine SiC surface and was considerably stable even after 100 h time on stream DRM reaction. The CNFs decorated SiC composite support provided more anchorage sites for improving the dispersion of the Ni particles and enhanced the metal-support interaction compared to the pristine SiC support.

In chapter 2, Iron-based Fischer-Tropsch synthesis (FTS) has received renewable interests due to the gradual depletion of crude oil resources and its flexible product adjustment from lower olefins to long-chain hydrocarbons. However, one of the main challenges of iron-based FTS catalysts is the relative lower activity or productivity (per gram catalyst) at low or middle temperature. In this work, ultra-active iron-based FTS

catalysts (Fe/SMC) were developed by loading iron over spherical mesoporous carbon (SMC) with huge porosity. The large pore volume and high specific surface area of SMC allowed the high iron loading (up to 50 wt%) with proper dispersion. Weak C-Fe interaction was observed in the Fe/SMC catalysts, which was favorable for the reduction of iron and its further carburization to form more active sites of FTS. Activity tests showed that the Fe/SMC catalysts exhibited ultra-high activities in FTS. With the increase of iron loadings (30-50 wt%), the FTS rates of Fe/SMC catalysts increased due to the larger iron surfaces exposed at higher iron loadings. Small amount of K promoter significantly enhanced the FTY and apparent turnover frequency of the Fe/SMC catalysts. The hydrocarbon productivity of K-promoted catalyst was up to 0.91 g HC/(h·g cat.) (260^{o}C, H_2/CO=1, 2 MPa), much higher than that of any other supported or unsupported iron-based FTS catalysts reported at similar reaction conditions.

In chapter 3, Superior iron-based Fischer-Tropsch synthesis (FTS) catalysts (Fe/NMCs) were developed by impregnating high amount of iron over nitrogen-rich mesoporous carbons (NMCs) with high porosities. The large pore volumes and specific surface areas of NMCs realized the high loadings and proper dispersions of iron while the nitrogen-containing groups enhanced the basicity of the catalysts. Weak metal-support interactions were observed in Fe/NMCs, which improved the reduction, carburization of iron, and further the FTS activities. FTS tests indicated a medium amount of nitrogen (≤ 8.3 wt%) did not show obvious effect on the activity of the catalyst, but a much higher amount of nitrogen (≥16.5 wt%) could result in a significant decrease of activity. The hydrocarbon productivity of the Fe/NMCs was up to 0.62 g HC/(h·g cat.) at 260 ^{o}C, 1 MPa, and H_2/CO ratio of 1, much higher than that of any other iron catalyst reported under similar conditions.

【論文審査の結果の要旨】

当学位審査委員会は本論文を詳細に審査し、かつ論文審査会を平成 30 年 8 月 22 日公開で開催し、その発表と質疑応答について審査した。その審査結果を下記のようにまとめる。

石油代替燃料製造において、シェールガス（天然ガス）、石炭あるいはバイオマスから合成ガス（一酸化炭素と水素の混合ガス）を経由する製造ルートは最も有力である。本論文は天然ガスから合成ガスの製造；合成ガスから軽油の製造を研究しており、それぞれの化学反応に最適な新規触媒の研究と開発を行った。

本論文は緒言とまとめ以外、三章から構成されている。

第一章は天然ガスと二酸化炭素から合成ガスの製造用触媒に関する研究である。このメタンと二酸化炭素転換反応プロセスに合わせて、優れた伝熱能力と強度を有するモノリス一型炭化ケイ素を触媒担体としたが、触媒担体の比表面積が不足しているので、モノリス一型炭化ケイ素ペレット表面に触媒成長法によって更に炭素ナノファイバー(CNF)を成長させ、高い比表面積を実現できた。この複合触媒担体へニッケルを担持し、Ni-CNF/monolith-SiC 複合触媒を調製した。新規調製法で得られたこの触媒が高い活性を示し、長い触媒寿命も達成した。更に各種の物理・化学分光手法を用いて新規触媒調製法のメカニズム、並びに触媒反応のメカニズムを解明した。

第二章は合成ガスから軽油の製造(Fischer-Tropsch 合成；FT 合成)に関する研究である。FT 合成用触媒として鉄触媒が安価のため、工業生産用触媒として広く使われているが、沈殿法で調製されているため、触媒の比表面積が低く、高い生産速度を達成できない。本研究は市販樹脂を用いて、炭化など物理・化学的な処理を行い、大きな比表面積および大きな細孔容積を同時に有する球状メソ細孔炭素(SMC)ペレットを調製できた。SMC に鉄とカリウムを担持後、FT 合成において世界最高な反応能力を実現した(1kg 触媒 1 時間あたり 910g 液体油生産)。大きな比表面積、大きな細孔容積と大きなナノ細孔を同時に有し、素早い物質移動速度と高速触媒表面反応を両立できたことが、この世界最高な反応能力を実現できた原因であると解明した。

第三章は第二章の触媒に対する改善である。カリウムのみでは触媒の塩基性が足りないので、SMC 担体製造用樹脂原料を有機窒素も含む樹脂に切り替え、窒素を含む大きな比表面積および大きな細孔容積を同時に有する球状メソ細孔炭素ペレット(NMC)を調製できた。鉄とカリウムを NMC に担持してから触媒として FT 活性をテストした結果、触媒の還元性が大幅に改善され、生成物の選択性も向上された。更に各種の物理・化学分光手法を用いて新規 NMC 系触媒調製法のメカニズム、並びに触媒反応性能向上のメカニズムを解明した。

上記の内容は国際学術専門誌に原著論文 3 報として掲載された。

当審査委員会は以上を総合的に判断した結果、審査論文は、エネルギー、環境、無

機化学合成、触媒調製諸分野において、学術的価値のある知見を与えていると判断し、博士の学位論文として十分な価値を有し、博士の学位を授与するに値する論文であると判定した。